“Solubility” Is Not a Constant of a Substance: What Is Constant Is the Product

— Silver chloride dissolves to $\mathbf{1.330413 \times 10^{-5}}$ M in pure water, but to $\mathbf{1.770000 \times 10^{-7}}$ M with only $\mathbf{0.001}$ M of chloride present and to $\mathbf{3.218182 \times 10^{-10}}$ M in seawater at $\mathbf{0.55}$ M — the separator is whether the same ion is already present — [Paper 677]

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September 2026

— From thinking to syncing. —

Abstract

Solubility is listed in tables as a property of a substance. But the same substance dissolves four orders less when the same ion is already in the water.What is constant and what is not is counted, starting from the solubility product.No new theorem or law is claimed. First, and this is the core. The same salt dissolves four orders differently according to its surroundings——silver chloride gives $\mathbf{1.330413 \times 10^{-5}}$ M in pure water and only $\mathbf{3.218182 \times 10^{-10}}$ M in seawater (chloride at 0.55 M), a factor of $\mathbf{2.418934 \times 10^{-5}}$ (Section 2). **Second, a little of the common ion already moves it by orders——with chloride at 0.001 M it is 1.770000×10^{-7} M and at 0.01 M it is 1.770000×10^{-8} M, falling in inverse proportion** (Section 2). **Third, what is constant is the product——in every case the product of the silver and chloride concentrations stays at the solubility product 1.770×10^{-10}; only the division between them moves** (Section 2). **Fourth, the same numerical product means different solubilities for different types——for an AB salt it is 1.330413×10^{-5} M, and for an AB_2 salt with the same number it would be $\mathbf{3.537022 \times 10^{-4}}$ M, $\mathbf{26.585885}$ times as much** (Section 3). **Fifth, there is an effect in the other direction too——adding salts that share no ion lowers the activity coefficient: at an ionic strength of 0.1 M it is $\mathbf{0.690303}$ for a singly charged ion, and the apparent solubility rises by $\mathbf{1.448638}$** (Section 3). **Sixth, the separator is whether the same ion is already present ——if it is, the solubility falls; if unrelated salts are added, it rises** (Section 4). **Keywords**: solubility product, common-ion effect, solubility equilibrium, activity coefficient, ionic strength, sparingly soluble salt.

Scope of this paper (scope note): **No new theorem or law is claimed——the solubility product, the common-ion effect and the Debye--Hückel limiting law are all standard (Atkins and de Paula 2014, Harris 2015).Complex ions are not treated——that an excess of chloride redissolves the salt by forming complexes is not included. Only the simple solubility product is examined.Temperature dependence is not treated——only values at 25 degrees Celsius are used, and the solubility product moves with temperature.Activity coefficients are not derived——the Debye--Hückel limiting law is taken as given, and nothing is claimed beyond its range of dilute solutions.Analytical methods are not discussed——precipitation titration, gravimetric analysis and the actual composition of seawater are not the subject.Relation to earlier papers**: **Paper 443 showed that the rate of browning is set less by temperature than by water activity, the surroundings, and counted a factor of 11.9334 on taking water activity from 1.0 to 0.65——there a rate was a function of the surroundings; here an equilibrium is. Both show a number listed in a table to be a function of what is around it.**What is added is **setting the dissolved amount against the concentration of the common ion**, **putting the seawater-to-pure-water ratio at one part in 41340.5**, **showing that the same numerical product gives solubilities 26.585885 times apart for different types**, **placing the activity-coefficient effect as the other side of the boundary**, and **placing the separator on the presence of the common ion**.

1. Notation and the Question

Setting: **a sparingly soluble salt AB dissolves into A^{+} and B^{-}. At equilibrium the product of the two concentrations is fixed.**

$$K_{sp} = [\mathrm{A}^{+}][\mathrm{B}^{-}], \qquad s_{\text{pure}} = \sqrt{K_{sp}}, \qquad s_{\text{common}} = \frac{K_{sp}}{[\mathrm{B}^{-}]}$$

For silver chloride the solubility product is 1.770×10^{-10} at 25 degrees Celsius.

Question: **is “solubility” a constant of the substance, or a function of its surroundings?**

2. Four Orders with the Surroundings

Computation 2.1: **the dissolved silver was derived for each chloride concentration.**

chloride	dissolved silver	against pure water
0 M (pure water)	1.330413×10^{-5} M	1
0.001 M	1.770000×10^{-7} M	1.330413×10^{-2}
0.01 M	1.770000×10^{-8} M	1.330413×10^{-3}
0.1 M	1.770000×10^{-9} M	1.330413×10^{-4}
0.55 M (seawater)	3.218182×10^{-10} M	2.418934×10^{-5}

In seawater it is one part in 41340.5 of the value in pure water. By mass, 1.906749×10^{-3} g per litre becomes 4.612298×10^{-8} g.

> **Observation 2.2**
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> this is the core: the division moves and the product does not.In every row the product of the silver and chloride concentrations stays at 1.770×10^{-10}. Where chloride is plentiful, the silver side must come down to satisfy that product——what is constant is the product, not the solubility.

3. Type, and the Opposite Effect

Computation 3.1: if an AB_2 salt carried the same numerical solubility product, its solubility would be $(K_{sp}/4)^{1/3}$, that is 3.537022×10^{-4} M, 26.585885 times that of the AB salt.

> **Observation 3.2**
>
> the number alone does not allow a comparison.The same 1.770×10^{-10} gives solubilities 26.585885 times apart according to how many ions the salt divides into——one may read “this one is less soluble” off a table of products only when the types match.

Computation 3.3: for salts sharing no ion, the Debye--Hückel limiting law gives, for a singly charged ion, activity coefficients of 0.963616 at an ionic strength of 0.001 M, 0.889406 at 0.01 M and 0.690303 at 0.1 M, raising the apparent solubility by 1.037758, 1.124346 and 1.448638.

Observation 3.4

the surroundings act in two directions.More of the same ion lowers the solubility; more of an unrelated salt raises it through the ionic strength——both are the same fact, that the value is a function of the surroundings, with opposite signs.

4. The Separator

Observation 4.1

the separator is whether the same ion is already present.If it is, the condition on the product pushes the silver side down; if the added salt shares no ion, activities fall and dissolving becomes easier——the single word “solubility” hides both effects at once.

Observation 4.2

beside Paper 443.Paper 443 showed that the rate of browning is set by water activity rather than temperature, counting a factor of 11.9334 from 1.0 to 0.65——there a rate was a function of the surroundings; here an equilibrium is. Both are cases where a tabulated number means nothing on its own.

Observation 4.3

what is not said.Complex ions and temperature dependence are not treated, and the activity coefficients hold only within the limiting law——what is shown is that the product is the constant, and that solubility moves four orders with the surroundings.

5. Roll Call and Closing

1. $\mathbf{1.330413 \times 10^{-5}}$ **M in pure water** (Computation 2.1): **the tabulated value.**
2. $\mathbf{3.218182 \times 10^{-10}}$ **M in seawater** (Computation 2.1): **the core.**
3. **a factor of** $\mathbf{2.418934 \times 10^{-5}}$ (Computation 2.1): **one part in 41340.5.**
4. $\mathbf{1.770000 \times 10^{-7}}$ **M at 0.001 M** (Computation 2.1): **a little common ion.**

5. **the product stays 1.770×10^{-10}** (Observation 2.2): **the constant.**
6. **AB_2 gives 3.537022×10^{-4} M** (Computation 3.1): **same number, other type.**
7. **a ratio of 26.585885** (Computation 3.1): **tables cannot be compared directly.**
8. **activity coefficient 0.690303** (Computation 3.3): **at 0.1 M ionic strength.**
9. **apparent solubility 1.448638 times** (Computation 3.3): **the opposite direction.**
10. **is the same ion present** (Observation 4.1): **the separator; Paper 443.**

Closing: **Solubility is not a constant of a substance.Silver chloride gives 1.330413×10^{-5} M in pure water and only 3.218182×10^{-10} M in seawater, one part in 41340.5.In every case the product of the two ion concentrations stays at 1.770×10^{-10}, and only the division between them moves——the constant is the product.With the same number, an AB_2 salt would dissolve 26.585885 times as much, and unrelated salts lower the activity coefficient to 0.690303 and raise the apparent solubility by 1.448638——a tabulated number means nothing without saying what is around it.The separator is whether the same ion is already present.Placed among the earlier papers——in Paper 443 a rate was a function of the surroundings; here an equilibrium is.To be honest——complex ions and temperature dependence are not treated, and the activity coefficients hold only within the limiting law.**

References

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